



DEPARTMENT OF THE NAVY

ENGINEERING FIELD ACTIVITY, NORTHEAST
NAVAL FACILITIES ENGINEERING COMMAND
10 INDUSTRIAL HIGHWAY
MAIL STOP, #82
LESTER, PA 19113-2090

IN REPLY REFER TO

5090
Code EV23/CF
March 13, 2006

Ms. Kymberlee Keckler, Remedial Project Manager
Federal Facilities Superfund Section
USEPA Region 1
1 Congress Street, Suite 1100
Boston MA, 02114-2023

Mr. Paul Kulpa, Project Manager
Office of Waste Management
Rhode Island Department Of Environmental Management
235 Promenade St.
Providence Rhode Island, 02908-5767

Dear Ms. Keckler / Mr. Kulpa:

SUBJECT: DRAFT SEDIMENT AND GROUNDWATER MONITORING REPORT AND
APPENDIX E - HYDROCARBON CHARACTERIZATION REPORT, (JULY
2005) FOR SITE 09, OLD FIREFIGHTING TRAINING AREA,
NAVSTA NEWPORT, NEWPORT RHODE ISLAND

The Navy's responses to EPA and RIDEM comments on the
subject report are provided as enclosures (1) and (2).
Enclosures (3) and (4) comprise the literature articles
requested in RIDEM Comment No. 54.

As stated in these responses, many of the RIDEM comments
show a general lack of confidence in the overall concepts of the
forensic analysis. These comments were carefully considered,
and although the comments have caused us to make some changes to
the report, the report conclusions stand as previously stated.
The Navy considers this type of effort part of the scientific
process and will continue to consider hydrocarbon
characterization an important part of the site cleanup process
at this and other sites where it is appropriate.

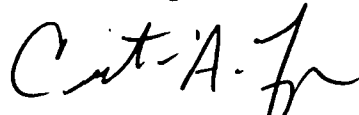
In accordance with these responses, the Sediment and
Groundwater Monitoring Report will be finalized. Responses to
separate RIDEM comments on the Sediment and Groundwater Report
were provided under Navy cover letter dated December 7, 2005.

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As stated in previous correspondence, the Sediment and Groundwater Monitoring Report and its Appendicies are key documents for the review being conducted by the OFFTA Optimization Review Team. The Navy will be seeking to set up a meeting to discuss the review team's findings in April.

If you have any questions, please do not hesitate to contact me at (610) 595-0567 x142.

Sincerely,



CURTIS A. FRYE, P.E.
Remedial Project Manager
By Direction of the
Commanding Officer

Enclosures:

1. Responses to EPA Comments, Draft Sediment and Groundwater Monitoring Report, Site 009, Old Firefighting Training Area, Naval Station Newport, Newport, RI, July 2005 (Comments dated December 22, 2006)
2. Responses to RIDEM Comments, Appendix E to the Draft Sediment and Groundwater Monitoring Report, Site 009, Old Firefighting Training Area, Naval Station Newport, Newport, RI, July 2005 (Comments dated November 30, 2006)
3. Stout et al, Comparative Evaluation of Background Anthropogenic Hydrocarbons in Surficial Sediments From Nine Urban Waterways. Env. Sci. Technol. 2004, 38, 2987-2994
4. Spawar Systems Center San Diego (SSC), 2003. A User's Guide for Determining the Sources of Contaminants in Sediments. Technical Report 1907. September 2003.

Copy to:

C. Mueller, NSN
S. Parker, TtNUS
J. Stump, Gannett Fleming
K. Finkelstein, NOAA

**Responses to Comments from the USEPA
On Navy Correspondence Dated September 7, 2005
Re: OFFTA Sediment and Groundwater Monitoring Report (TtNUS 2005),
and Hydrocarbon Characterization Report (Newfields, July 2005)**

(EPA Comments Dated 12/22/05)

Sediment and Groundwater Monitoring Report

EPA Comment on Navy Response 4:

The general trend in PAH concentrations appears accurate as presented in the table when doing a point comparison using the sample dates presented. However, there are other sample dates presented in Table 4-3. The response specifies that only surface sediment samples are presented in Table 1. Until the sediment sample depths are added to Table 4-3, it is not readily apparent that Table 1 is comprehensive and consistent with data in Table 4-3.

Navy Response: Comment Noted. This information will be added to the tables in the revised report.

Hydrocarbon Characterization, Appendix E

EPA Comment on Navy Response 1

The comment requests clarification of the distinction between OFFTA-generated pyrogenic PAHs and pyrogenic PAHs from other sources, as well as a clear explanation of the methodology used to make this distinction. The Navy's Response provides a summary of the 'lines of evidence' approach that comprises the forensic analysis (paragraph 3 of this Response) and a succinct summary of the results (paragraph 4). I recommend that this Response be incorporated into the Executive Summary and the Introduction of the report. This additional text will aid the reader in understanding better the report's primary objective (to determine the relationships among hydrocarbons in sediments from Coasters Harbor, a Reference Area, and the OFFTA), and how the report's conclusions are supported by the forensic analysis.

Navy Response 1.1 The use of multiple lines of evidence in the forensic interpretation will be reiterated in several parts of the report (including the Executive Summary and Technical Approach sections) as recommended. The succinct summary will be added to the Executive Summary as recommended.

Please note that the last sentence of this Response reads, "Additional reference samples of will be added from other forensic investigations." I assume that Navy intended to refer to additional samples of specific materials. Please include this information in the revised report.

Navy Response 1.2 The final revision of the report will include data from many additional sediment samples collected from Narragansett Bay Reference Area locations in 2004 as part of the Allen Harbor and Derecktor Shipyard investigations. These data demonstrate the range of PAH sources within the Narragansett Bay region and help explain the subtle variation of the PAH signatures in sediment samples collected from Coasters Harbor.

The final revision of the report also will include data from many Reference Material samples of petroleum and tar products from other forensic projects. These data help benchmark the types of PAHs derived from fuel oils, used lubricating oil, coal tar, and pavement samples.

EPA Comment on Navy Response 2

EPA requested the inclusion of a section addressing the various sources of uncertainties associated with this study, and an assessment of the effects of these uncertainties on the investigation's conclusions. The Response indicates that the report will be revised to include a discussion of the laboratory QC results "...as part of an uncertainty analysis." The comment asked the Navy to address all sources of uncertainty, in addition to laboratory QC issues. For example, the first paragraph of the Response states that "...these reference samples provide performance data on most of the target analytes used throughout this forensic investigation." Are there target analytes for which reference samples do not provide performance data? How are differences in regional hydrocarbon signatures in reference area samples to be addressed? Please ensure that the uncertainty analysis in the revised report acknowledges any other 'unknowns' and states clearly how this information is used and evaluated in formulating the conclusions.

Navy Response

The final revision of the report will discuss the QC performance associated with the forensic results. This evaluation establishes the high degree of accuracy and precision of the analytical results used to form conclusions about the possible origins of hydrocarbons in Coasters Harbor. The variance in QC samples, like the sample duplicates, blind field duplicates, and crude oil samples in the PCA plots (Figure 5) provide an adequate quantity of information to demonstrate that the hydrocarbon signatures can be reliably identified and traced in the environment with the reported forensic data and associated report. It is recommended that concerns about additional sources of uncertainty be articulated and discussed in subsequent conference calls or meetings.

EPA Comment on Navy Response 5

The sediment containing the horizons with the proper time frame associated with OFFTA operational history has not been identified. The uncertainty associated with not sampling, or accurately knowing, the correct depth of deposition should be addressed in the uncertainty section.

Navy Response

The sampling depth was originally established by the Navy based on the goals of the risk assessment. For monitoring purposes, similar depth intervals were collected for comparison. Deeper sediments were not considered relevant for evaluating risk or contaminant origins. The PAH deposition dates are not a focus of this study.

EPA Comment on Navy Response 8

The comment questioned the limited number of reference/background locations and samples that were used to characterize the regional background hydrocarbon signature. Navy's Response states that data from additional reference area samples (from Coggeshall Cove, Jamestown Island, and Fishing Cove), from the Davisville Sediment Investigation, will be added to this report. Please explain the rationale for the total number of additional reference area samples and explain why Navy considers the total number adequate to meet the study objectives.

Navy Response 8.1 The rationale for additional Reference Area sediment samples is based on the typical diversity of PAH inputs to a large and complex system like Narragansett Bay. The over-reliance on a single Reference Area, such as Jamestown Potter Cove (JPC), potentially under-represents the contribution of PAHs from north and south of the study area. Likewise, the exclusive use of JPC Reference Area sediment samples may not represent the difference in PAH inputs from rural and urban background locations around Narragansett Bay.

The final revision of the report will demonstrate the utility of using multiple Reference Areas to determine the types of PAH signatures attributable to background samples. Specifically, Figure 5 will compare Coasters Harbor sediments with different Reference Areas and Reference Materials. These results demonstrate the high degree of consistency among Coasters Harbor sediments, Reference Area sediments, and many pavement Reference Materials. The positive association among these samples contrasts with the compositional features of fuel oils, crude oils, and lubricating oils.

The Navy's response suggests that some differences in hydrocarbon compositions and concentrations within the reference area data are to be expected, because of differences in density of roadways and land use in the Newport area. Please ensure that the uncertainty section in the revised report discusses the sources and magnitude of variability within the reference area data set.

Navy Response 8.2 The magnitude of variability among Reference Area samples will be demonstrated in Figure 5 of the final revision to the forensics report.

EPA Comment on Navy Response 14

EPA requested an expansion of the discussion comparing pyrogenic PAHs attributed to pavement samples along the shoreline adjacent to the OFFTA and those from combustion of the various fuels that were used at the OFFTA. The response states that the report will be revised to include a brief discussion of differences between sediments and combusted fuel samples. In revising the report, please keep in mind the sources of uncertainty that are alluded to in this response (e.g., historical generation of pyrogenic PAHs during OFFTA activities, mass-balance estimates, effects of dilution, etc.) and address these accordingly.

Navy Response A new section (Attachment H) of the final report will describe the petroleum products commonly encountered during environmental investigations. It will include the diesel range middle distillate for which past use at the OFFTA is well established. It also will include other fuels that were used in naval vessels, but whose use was not established at the OFFTA; e.g., kerosene and heavy fuel oil. Samples of historical pavement will be also featured in Attachment H to help illustrate the types of heavy petroleum and tar used to manufacture roadway materials. These pavement samples resemble well the composition range of pavement samples collected on the OFFTA shoreline and PAHs measured in the Coaster Harbor sediments.

With respect to the combusted fuel samples, Attachment H will correct an error in the initial report. The fuel combustion study reported originally reflected the use of crucibles that were previously used as part of a tar ashing project. As a result, these samples were contaminated with pyrogenic PAHs. The experiment was repeated by Battelle in 2003 using new crucibles. The results from this study

were used in the final revision of the report (Attachment H and Figure 5). These uncontaminated fuel samples did not contain pyrogenic PAHs as discussed in Attachment H. The fuel residues contained petrogenic 2- to 4-ring PAHs that exhibited a progressive loss of lighter hydrocarbons as the fuel was consumed. These PAHs could not environmentally weather into pyrogenic 3- to 6-ring PAHs that were widely observed in the Reference Area and Coasters Harbor sediments. Therefore, it was highly unlikely that the fuel residues from the OFFTA activities comprised a significant source of pyrogenic PAHs in the offshore sediments.

**Responses to Comments from RIDEM on
Appendix E to the Draft Sediment and Groundwater Monitoring Report,
Old Fire Fighting Training Area
Comments Dated 11/30/06**

General Comment:

The Rhode Island Department of Environmental Management, Office of Waste Management has reviewed the Sediment and Groundwater Monitoring Report, Old Fire Fighter Training Area. In previous correspondence and meetings, the Office of Waste Management raised a number of concerns with respect to the validity of the original forensic study performed at the site and the conclusions generated by that study. These concerns were never addressed by the Navy. Accordingly, the Office of Waste Management could not approve the report and stated that conclusions presented in that study could not be used as a foundation for decisions made at the site. The Navy then proposed to perform a second similar study. At that time the Office of Waste Management noted that it's position concerning this matter had not changed and did not approve the proposal to perform a second similar forensic study. The Navy elected to perform the second study using procedures and protocols, which had been questioned and found unacceptable in the first study. This brought into question the need for this agency to review the second forensic study. However, at the recommendation of the US EPA and the Navy the Office of Waste Management has generated comments on the forensic portion of the Sediment and Groundwater Monitoring Report, Old Fire Fighter Training Area.

Response:

The comment is noted. Review of our records shows that the first forensic report was prepared for the subject site dated September 2002 and RIDEM provided comments on that report November 15 2002. In early 2003, a meeting was held at RIDEM's office to describe the results and findings of that report, and to address RIDEM's concerns regarding that study during the meeting. At the conclusion, it is our recollection that there were no further comments from RIDEM.

Regardless, it is the Navy's obligation and intention to continue to investigate and address the site in the manner deemed suitable based on all the information available. The forensic hydrocarbon analysis is integral to determining and addressing the site related risks without damaging a healthy ecosystem that contains anthropogenic contaminants.

Many of the specific comments addressed below show a general lack of confidence in the overall concepts of the forensic analysis. We are developing a revised document based on the comments, with basic concepts described in detail, additional reference material analysis and other support information. It is our hope that this revision will address most of these comments.

It should also be noted that the US EPA has also reviewed the subject document and provided suitable comments which also will direct modification of this document.

Specific Comments:

**1. Introduction,
Paragraph 1.**

Typical of other firefighter training areas across the country, waste oils were used at the site. This was noted in the first report performed on the site, the Initial Assessment Study. Therefore, please modify this section of the report to state that waste oils were used at the site.

Response:

The only known hydrocarbon materials used at the site were diesel fuel marine (a middle distillate with manufacturing specifications that largely overlap with regular diesel and #2 fuel oil) and pavement.

Despite the unknown occurrence of kerosene and heavy fuels at the OFFTA site, Reference Material samples of equivalent petroleum products were added to the final revision of the report. The results of these analyses demonstrated that these materials were not evident in the Coasters Harbor sediments. The presence of waste oil in the soil is not confirmed by the studies conducted to date.

**2. Introduction,
Paragraph 1.**

This section of the report notes that candidate fuels include jet fuel, kerosene, marine diesel and boiler range heavy fuel oil. Jet fuel was not used by the military during WW II. High-octane aviation fuel would have been used. In addition, the Navy used both Navy Special and Navy Black oil for their surface ships. Please modify this section of the report to include these fuels.

Response:

The only known hydrocarbon materials used at the site were diesel fuel marine (a middle distillate with manufacturing specifications that largely overlap with regular diesel and #2 fuel oil) and pavement.

Despite the unknown occurrence of kerosene and heavy fuels at the OFFTA site, Reference Material samples of equivalent petroleum products were added to the final revision of the report. The results of these analyses demonstrated that these materials were not evident in the Coasters Harbor sediments.

Jet fuel would have been used post WWII, and the OFFTA was in operation at that time. Further discussion on the sources of fuels and their constituents will be included in the revised report.

**3. Technical Approach,
Paragraph 1.**

Potential candidate sources of contamination are listed in this paragraph. In regards to the fire fighter training area the report should note that there was at least one oil water separator at the site, which discharged into the bay, as well as tanks for underground storage of the fuel oils. The report must depict the locations of the discharge lines from the oil water separator(s) on a figure, as well as the underground tanks and associated piping network for the tanks.

Response:

The figure requested is provided in the Remedial Investigation Report, part of the administrative record for this site.

**4. Technical Approach,
Paragraph 1.**

A review of engineering plans reveals that a series of storm drains, other than the two depicted in this report, cross the site. In addition, storm drains serviced the Fire Fighter Training Area itself. When the site was active these drains would have served as likely discharge points from operations associated with the Fire Fighter Training Area. Currently, they would serve as preferential flow paths for groundwater contamination. The report must include a discussion of these drains and depict their locations on a map.

Response:

Current storm drain configurations are provided on Figures 4-1, and 4-2 of the parent report, the Sediment and Groundwater Monitoring Report.

**5. Technical Approach,
Paragraph 1.**

There are sanitary sewer lines which crossed the site. These lines would serve as preferential flow paths for contaminants in the groundwater. The report must include a discussion of these lines and depict their location on a map.

Response:

There are currently no known sanitary sewer lines at the site.

**6. Technical Approach,
Paragraph 1.**

Please include in an appendix a copy of the field notebooks used when the samples were collected.

Response:

Sample collection records are provided in Appendix A of the parent report, the Sediment and Groundwater Monitoring Report.

**7. Technical Approach,
Paragraph 2.**

This section notes that two samples of asphalt from the shoreline were analyzed. Please provide more details concerning these asphalt samples. That is were the samples composed of asphalt and sand, or pure asphalt (pieces of asphalt). Also, it appears that one sample contained a binder. Please confirm and describe the binder.

Response:

The debris samples were both individual pieces of asphalt, approximately four inches in diameter and are described on sample log sheets provided in Appendix A of the parent report.

**8. Technical Approach,
Paragraph 2.**

This section of the report notes that reference samples included crude, kerosene and diesel. The chromatograms from these fuels were compared to site samples. A cursory review of fuels used by the Navy would reveal that aviation fuel, jet fuel and Navy Special were used as fuel sources. In addition, waste oils would have been burned at the site. This should be noted in this section of the report. Further, samples of these fuels must be employed as reference samples.

Response:

Comment noted. Please refer to the responses to comments 1 and 2 above. Additional discussion on fuel sources will be provided in the revised report, and additional reference material tests will be added to the report as supporting information. These include heavy fuels and motor oil.

**9. Technical Approach,
Paragraph 2.**

This section states that oils in various stages of weathering were employed. Please describe how oils in various stages of weathering were obtained. That is, were soils contaminated with these fuels from other sites used in this analysis, were fuels artificially aged, and if so how were they artificially aged?

Response:

This section of the report will be revised for clarity.

**10. Technical Approach,
Paragraph 2.**

Only a limited number of weathered fuel samples was used in this analysis. Since a variety of oils was used at the sites, weathered samples of aviation fuel, jet fuel, waste oil and Navy Special must also be included in this analysis.

Response:

Comment noted. Please refer to the responses to comments 1, 2 and 8, above. Additional discussion on fuel sources will be provided in the revised report.

**11. Technical Approach,
Paragraph 2.**

At the Old Fire Fighter Training Area a variety of fuel oils and waste oils were used in the fire fighting training exercises. This would have resulted in releases of the oils themselves, as wells as partially combusted and/or heated oils. Therefore, the forensic analysis would have to evaluate partially combusted and/or heated oils and waste oils.

Response:

Comment noted. Please refer to the responses to comments 1 and 2 above. Additional discussion on fuel sources (including motor oils) and findings will be provided in the revised report.

**12. Technical Approach,
Paragraph 2.**

The intent of the study was to determine whether the chromatographs fingerprint of the sediments were indicative of onsite sources, i.e. firefighter operations, or normal background. In the current study the Navy elected to resample sediment and catch basin samples that previously underwent analysis in the original forensic study. However the Navy did not resample onsite soils in the current study. Please explain why it was necessary to resample sediment and catch basins samples, but is was not necessary to resample onsite soils.

Response:

The chromatographs of the soil samples collected during the soil pre-design investigation are being evaluated for inclusion and will be discussed in a new section, Attachment I.

**13. Technical Approach,
Paragraph 2**

In the current study no onsite soils underwent forensic analysis. In the previous study only two onsite soils underwent forensic analysis. Based upon observations from test pit logs and soil borings it is known that contamination at the site is not homogenous. That is, in some sections of the site heavy oils were found at other locations lighter oils were found and/or a mixture of oils were present. The heterogeneity of the site was also demonstrated by the two vastly different chromatograms that were obtained from soil samples collected at two locations that underwent analysis in the first forensic study. Since it is known that the site is heterogeneous and the collection of only two samples during the first forensic study was found to be insufficient, additional samples should have been collected in this study. Therefore, additional onsite soil samples must be collected from the site. It is recommended that onsite soils which exhibited visual or olfactory evidence of contamination from known areas of contamination be selected for analysis.

Response:

Soil analytical chromatographs from the soil predesign investigation are being evaluated for inclusion and will be discussed in a new section, Attachment I.

**14. Technical Approach,
Paragraph 2.**

In the current forensic study onsite soils did not undergo forensic analysis. Instead, the results from the previous forensic fingerprints of onsite soils were referenced. Typically, in order to compare chromatograms in a forensic analysis, the same procedures must be employed. Specifically sample prep, and the type of column used, operating parameters associated with the columns, flow rates, temperature ramps, detectors, etc must be the same. In order to use the results from the previous analysis the report must include a table which outlines each step of sample prep for both analyses and each operating parameter for the GC in both analyses. Differences, between the two preps and GC analyses must be highlighted and discussed. Finally, as the final test of the comparability of the two studies, the chromatograms of the catch basin and sediment samples taken in both studies must be compared and any differences in elution time, fingerprint, etc must be explained.

Response:

Two additional attachments will be added to the forensic report, Attachment G, which is a quality control sample summary, and Attachment H, an overview of the process followed which should address this comment. In addition, soil analytical chromatographs from the soil predesign investigation are being evaluated for inclusion and will be discussed in a new Attachment I.

**15. Technical Approach,
Paragraph 2.**

The current forensic study elected to use the chromatograms from soil samples collected in the first forensic study. However, it does not appear that the actual chromatograms were included in the report. Assuming that the chromatograms can be used (see above comment), the report must include the chromatograms in the appendix.

Response:

Refer to the response to comment 14 above. The soil chromatograms are being evaluated for inclusion and discussion in a new Attachment, Attachment I, which will address this comment.

**16. Technical Approach,
Paragraph 2.**

The study relies on high-resolution chromatographic analysis of site samples and reference samples. For each sample please specify the operating parameters, (GC temperature ramp, flow rates, etc). If the samples were run under different conditions or using different GC or columns this should be noted and the information should be provided in a table.

Response:

Some of the information requested is presented in Attachment F (laboratory report). However, two additional attachments will be added to the forensic report, Attachment G, which is a quality control sample summary, and Attachment H, an overview of the process followed. The addition of this information will address this comment.

**17. Technical Approach,
Paragraph 2.**

The crux of the Navy's position is that the highest concentration of PAHs was observed at the outfalls and the source of the PAHs is typical urban runoff. An alternative explanation, which early studies had indicated, was either input of contaminants from the site directly into the storm drains and /or preferential flow paths of contaminants from this site along the storm drains. If the source of the PAHs was typical urban runoff, as opposed to site related PAH, one would also find that the highest concentrations of metals typically observed in urban runoff, such as nickel and copper would be found at the outfalls sediment samples. A review of the data reveals that this is clearly not the case. Significantly higher concentrations of these metals are found

away from the outfalls. This fact would point to the PAHs being site related and not urban runoff related. Please include a discussion of these facts in the report.

Response:

The fate and transport properties of petroleum hydrocarbons and metals are different. There is little reason to expect that concentrations of hydrocarbons and metals would follow similar pathways. The report does not evaluate the concentrations or distribution of metals in the sediment. This could be the subject of yet another line of evidence to evaluate on this topic.

**18. Technical Approach,
Paragraph 2.**

In general, any forensic analysis of the site would have to address the problem that a variety of fuels were used at the site, including waste oils, and these fuels were exposed to heat and combustion. This would have resulted in releases of unburnt fuels, fuels exposed to heat and fuels exposed to combustion, all of which would have undergone physical/chemical/biological degradation. The first step in any forensic analysis would have been to determine whether one can even distinguish between the petrogenic/pyrogenic signatures associated with firefighting operations and petrogenic/pyrogenic signatures of urban background. This would have necessitated running samples of these fuels, as well as fuels exposed to heat and/or combustion and finally the various degradation processes. Once it has been established that one is able to distinguish between the two, then the forensic study could proceed. Without performing this initial, critical test, the study is unfairly biased and flawed and meaningful conclusions cannot be drawn. Accordingly, these additional tests need to be performed in order to determine whether a forensic analysis is even possible at the site.

Response:

There are two parts to the comment above. Regarding the first portion, a new section of the report will be provided to describe how the different signatures of the likely different source fuels are differentiated, after burning or degradation. This "first step" described above has been done, documented and evidenced in scientific literature describing forensic hydrocarbon analysis. It is the principal of the forensic science, and it was used to show the differences in the material found on site and off site in the 2002 study.

The comment suggests attempting to reconstruct activities at the site using the same source fuels and subject them to the same weathering processes that occurred in nature over a period of many years. This is an impractical approach to a simple problem that can be addressed through documented testing that has been provided and will be further supported with the additional reference information. The simpler and more effective approach to compare two materials is to test the two materials and identify their differences. This is what has been done for the forensic study.

The comment shows clear misunderstanding of the process and it is hoped that the new Attachment will address this misunderstanding.

**19. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 2.**

The report is a public document, therefore the concepts in this paragraph need to be clearly discussed. As an illustration, the report should explain what is meant by the organic residues of thermal decomposition (soot, creosote and tar based asphalt) and petroleum (diesel, heavy fuel oil and petroleum asphalt). The report should also state what are the upgradient or onsite sources of soot, creosote, tar based or petroleum based asphalt, etc

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, and will address this comment.

**20. Section 4.1, Dominant Hydrocarbon Signatures,
Paragraph 2.**

The report is a public document therefore statements that a particular range of PAHs or a particular PAH is associated with asphalt, diesel, etc., should be explained in detail. Further the bases for this statement should be provided and attached as an appendix or at a minimum the web address for the reference must be provided. Finally, please provide tables listing all of the PAHs associated with the different sources and typical concentrations.

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, and presents reference and standard materials described in the report. The addition of this Attachment will address this comment.

**21. Section 4.1, Dominant Hydrocarbon Signatures.
Paragraph 3.**

This paragraph states that the PAHs observed in the samples were associated with abraded asphalt from the parking lot. As this is a public document, please explain what is meant by abraded asphalt, that is, were pieces of asphalt found in the sample, etc.

Response:

Roadway pavement becomes brittle with age and use. As it degrades, small and large pieces detach from the roadway surface. During rain events, unattached particles wash off the roadways, into the storm sewers, and out into the receiving waters near the outfall. As the particles move with the storm water, the abraded pavement scrapes against other particles and break into smaller pieces. The small pieces combine with other soil and sediment particles and become difficult to identify physically. For this reason, forensic investigators use the molecular signatures of pavement and other site data to identify the presence of urban background constituents, like pavement, in the environment. The smoothed edges of the debris samples is testament to the presence of abraded pavement in the Coasters Harbor environment.

The debris samples (Debris 1 and Debris 2) were asphalt pieces, picked up from the shoreline and abraded for analysis. This would simulate the mechanical breakdown that occurs during wave action at the site.

**22. Section 4.1, Dominant Hydrocarbon Signature.
Paragraph 3.**

This paragraph references figure 3 that depicts the range of heavy fuel oils. The figure shows fuel oils stopping just short of C-40. Heavy fuel oils go to C-40 and beyond. Please modify the figure to reflect this fact.

Response:

The useful hydrocarbon range for the subject of the report is covered within the C-40 range. Additional discussion on this matter will be included in the final report.

**23. Section 4.1, Dominant Hydrocarbon Signature
Paragraph 3.**

This paragraph references figure 3 which contains chromatograms of debris 1 and 2 both of which contain asphalt. One chromatogram contains the UCM in the C 30-C40 range the other does not. Please explain.

Response:

The heterogeneity of the asphalt pieces is noted in the report. They could have been set at different periods, with different formulas. Additional discussion will be provided in the revised report.

**24. Section 4.1, Dominant Hydrocarbon Signatures
Paragraph 4.**

The chromatograms for the asphalt samples have considerable differences. In essence the Navy is suggesting that the chromatograms of asphalt can be vastly different. This complicates the investigation and is important as it has obvious implications when comparing chromatograms. To insure that the observed differences reflect different composition of asphalt, (as opposed to field, lab error, contaminants on asphalt, etc) and to ascertain whether other chromatographic fingerprints of asphalt are not possible, it is recommended that additional samples of asphalt be collected and analyzed.

Response:

Please refer to the response to comment 24 above. The debris samples were taken from the shoreline of the OFFTA site for the purposes described.

**25. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 4.**

The report notes that benthic and biochemical weathering does not occur in the insulated confines of the asphalt. Please explain this statement. Is the Navy stating that the exterior of a piece of asphalt that is exposed to weathering would have a different chromatogram from the interior, which is not exposed to weathering? If this case please provide a copy of the reference from the literature or a copy of the chromatograms taken on the exterior and interior of the asphalt, which supports this position.

Response:

The statement in question means that the exposed surface of the asphalt is subjected to different physical, chemical, and biological conditions that may affect the molecular makeup of the material on that surface. Taken in context with the rest of the paragraph, the point that is being made is that the material inside the asphalt is slightly different than the asphalt material found within the storm drains since it is still intact and unweathered, while the material in the storm drains is more weathered and exposed.

**26. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 4.**

PAHs were found in the sediments adjacent to the site. It is the Navy's position that the observed PAHs are from asphalt. Please state whether the contaminants found in these sediments represent PAHs, which leached from the asphalt or actual pieces of asphalt in the sediment samples.

Response:

To clarify, some of the PAHs in the sediment originate from asphalt, based on the testing conducted, and those PAHs would still be associated with particles of asphalt, tar, binder etc of all sizes. Please also refer to the response to comment 21, above.

**27. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 4.**

This report states that OFFTA 7 contained lightly degraded diesel and catch basin sample 75a contained heavily biodegraded diesel. Please provide the justification for this statement. This justification should include, but not be limited to, chromatograms of lightly and heavily biodegraded diesel.

Response:

This information will be provided as a new section (Attachment I) of the revised report.

**28. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 3.**

The report assigns the PAH distribution to asphalt and weather tar. The report must clearly and in detail provide justification for this statement. This justification should include, but not be limited to, chromatograms of all potential sources, a list of constituents found in these sources, a list of typical concentrations of PAHs in these sources, etc, an explanation of how one can distinguish between asphalt PAHs and PAHs associated with heavy fuel oils, burnt or combusted fuel oils, weathered fuel oils and fuel oils exposed to heat.

Response:

Additional discussion on this subject will be provided in the revised report.

**29. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 3.**

The report contains the chromatograms of three sediment samples collected from three storm drains. Even discounting the diesel signature in one of the drains, the chromatograms are not similar. Since the drains essentially served the same area, the chromatograms should have been nearly identical. Please explain in detail why irrespective of the diesel component in one sample, the chromatograms are not identical.

Response:

The report correctly cites possibilities of different asphalt materials in different areas laid at different times. The conclusions are made based on a preponderance of evidence described. Figures 3a through 3c show the UCM similarities. Chromatograms of different material will never be identical.

**30. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph 3.**

This section states that the chromatograms of the three catch basin samples contains middle distillate and soot or weathered tar byproducts. Justification for this statement must be included in the report. This justification must include chromatograms of soot or tar products, heavily weathered middle distillate, etc. The report must also clearly state how the observed distribution can be attributed to these sources as opposed to other petroleum products, including weathered products.

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, including additional reference material information. The addition of the new Attachment will address this comment.

**31. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph Whole Section.**

This section of the report attributes the PAH distribution in the sediments to asphalt, and roofing tar. The report is a public document, therefore it should clearly state whether the observed PAH distribution represents PAHs that have leached from asphalt, roofing tar, etc or reflects pieces of asphalt or roofing tar in the sediments.

Response:

The presence of the chemical constituents in the analytical results does not identify whether the material is present in particle form or has leached. The debris samples collected are abraded to scrape material from them, then the sample material is dried, shaken and extracted as described in Section 3.2 of the report. Please refer also to the response to comment 21, above.

**32. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph Whole Section.**

Please include a table with the concentration of the individual PAHs observed at the site, reference sediment samples, soil samples and the various reference samples, (i.e. crude oils, diesels, asphalt, Navy Special; waste oils, etc). The table should also highlight which PAHs are believed to be indicative of a particular PAH source in each sample, i.e. if sediment contains diesel PAHs this should be highlighted. Since the report is a public document the highlighted PAHs should be colored coded. That is asphalt PAHs would be one color, diesel PAHs would be another, etc. A designation should also be applied to PAHs that may be found in more than one source material.

Response:

The individual PAHs are not generally assigned to the specific sources as suggested in the comment above. The figures provided show mixtures of the different PAHs and other analytes. These mixtures, or patterns are what are used to determine sources and similarities.

**33. Section 4.1, Dominant Hydrocarbon Signatures.,
Paragraph Whole Section.**

This section of the report includes the results from the first forensic study. Prior to this study a forensic analysis was conducted on samples of pure asphalt, sediment mixed with asphalt and pure sediment with no asphalt. The results of this study must be included in the report and discussed in this section.

Response:

The specific report described in this comment is unclear. The ecological risk assessment report references a study by Battelle from 1994, which was largely rejected by the regulatory parties due to the use of composited samples. The findings of the 2002 forensic report conducted by Battelle are confirmed and refined somewhat in the 2005 forensic report by Newfields Inc.

**34. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2,**

The report is a public document, therefore please include a table delineates which PAHs are petrogenic, pyrogenic or both.

Response:

Specific PAHs are not assigned in a simplistic manner. Rather the specific mixtures of PAHs and relative concentrations are indicative of pyrogenic or petrogenic origins. A new section will be added to the report, Attachment H, which is an overview of the process followed for the work conducted, and will address this comment.

**35. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2,**

This section of the report makes statements concerning the relative abundance of alkylated and parent PAHs in petrogenic and pyrogenic samples. In support of this position, the report must include a series of chromatograms and tables depicting the typical distribution of these compounds from these sources . Be advised that the concentrations must also be included.

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, and will address this comment.

**36. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

This section of the report states that the presence of a particular compound is more important than the concentration of the compound due to interferences associated with phthalates, halogenated compounds and subtle chromatographic changes (peak widening) that can occur in a GC fingerprint. These statements are not applicable to this site. Halogenated organics were not disposed of at this site. In regards to phthalates the same equipment would have been used to collect all of the samples so phthalate contamination would have been consistent and further it would have been noted in the QA/QC process. If a chemist believes that a peak width is hiding critical components for PAH analysis, the solution is not to assume that this is occurring and therefore totally disregard concentrations. If this is important the solution is to run the sample again in such a manner as to achieve better separation and thus eliminate the effects of peak width widening. In consideration of the above the statement that PAH concentration can be discounted and the focus can be restricted to PAH distribution is not supported on this site. Doing so would bias any analysis. Therefore this portion of the forensic analysis must consider PAH concentration.

Response:

The text is not disregarding the PAH concentration, it is simply indicating that constituent pattern is more reliable than individual concentrations in determining the probable source of a material.

**37. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

Please include a table with the concentration of the individual PAHs observed in the site, reference sediment samples soil samples and the various reference samples, (petrogenic and pyrogenic , i.e. crude oils, diesels, asphalt, combusted crude oil diesel, etc). The table should also highlight which PAHs are believed to be indicative of a particular PAH source in each sample, i.e. if sediment contains petrogenic diesel PAHs this should be highlighted, if it contain pyrogenic PAHs this should be highlighted. Since the report is a public document, and to aid in the table interpretation, it is recommended that the highlighted PAHs be colored coded.

Response:

As stated earlier, the individual PAHs are not generally assigned to the specific sources as suggested in the comment above. The figures provided show mixtures of the different PAHs and other analytes. However, the new Attachment H, which is an overview of the process followed for the work conducted, will clarify this issue.

**38. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

This section of the report states that specific types of decaying vegetation contain certain PAHs. Please list these specific types of vegetation and note whether they were found at OFFTA.

Response:

Plants found at the site itself include cultivated grasses, and pine trees (up until 2004), and marine vegetation, including eelgrass and algal plants.

**39. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

This section of the report states that decaying vegetation contains certain PAHs, such as, perylene. Perylene is commonly found in diesel and # 2 fuel oil. Please explain how the presence of perylene can be attributed to decaying vegetation and not due to the presence of diesel or fuel oil.

Response:

A section on plant waxes is included as Section 4.3 (section 4.4 in the revised report). Again, the attributions are made based on present mixtures of materials not specific individual compounds and their concentrations.

**40. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

This section of the report discussed the sum of EPA PAHs observed in site sediments and the parking lot sediments. In order for the report not to be biased the concentration of EPA PAHs observed in site soil samples must be included.

Response:

A discussion of the soil results will be expanded and presented in a new Attachment I.

**41. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 2.**

The report notes that the concentrations of PAHs observed in the background stations is four to five times lower than that observed in the lowest PAH concentration site sample. A number of the samples were taken a considerable distance from the storm drains. Therefore, one would have expected to see concentrations equal to background. This is not the case. Therefore it is not appropriate to imply that observed PAH concentrations are background. Please remove these statements from the report.

Response:

Again, the composition of the PAHs present are more valuable for determining source of a material, than are concentrations alone. Concentrations of contaminants that are silt-borne materials are affected by physical characteristics of the area (whether it is a scouring area depositional area etc.). Coasters harbor is a depositional area which should be expected to trap more contaminant laden silts than most of the reference areas tested. Therefore, the comment is not correct at all, and concentrations should certainly not be equal to those measured in background. However, additional data from reference samples collected through other recent studies are being compiled for inclusion into the revised forensic report.

**42. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 4.**

This paragraph states that the high concentration of PAHs observed in the debris sample of asphalt provides credence for the position that abraded asphalt found in urban runoff is responsible for the high concentrations observed at the outfalls as opposed to the reference station, which has less urban traffic and less abraded asphalt. This theory is based upon speculation from sampling asphalt. A true test of this position would have involved testing of samples with and without asphalt. This was done in the past. The result was the theory that asphalt is the source of PAHs in the sediments was found not to be valid in an earlier forensics study performed at the site. In this study samples of asphalt, and samples of sediment mixed with asphalt and samples of sediment with no asphalt were analyzed. The lowest concentrations and the lowest number of PAHs was observed in the asphalt samples and samples of sediment mixed with asphalt. The highest concentration of and greatest number of PAHs were observed in the samples without asphalt. The report must include the results of this earlier study and remove all statements indicating that asphalt is the source of PAHs at the site.

Response:

The conclusions were gathered from the evaluation of the samples of asphalt itself, and they stand based on the data shown. It should be apparent that the Jamestown shoreline carries less automobile traffic than the Newport shoreline. The comment appears to further discuss the findings of a study by Battelle in 1994 (although without reference, so this is uncertain), which was largely rejected by the regulatory parties at that time (please refer to the response to comment 33 above).

43. Section 4.2, Petrogenic and Pyrogenic PAH Patterns., Paragraph 4.

This paragraph states that changes in land use over the past three years is responsible for the observed decrease in PAHs from the storm drains between the two sampling events. Please be advised that vehicle use increased at the site as a portion of Katy field was used as a parking lot starting in 2002. As such one would have expected to see an increase in PAHs, and not a decrease. Therefore, this statement should be removed from the report. Further, if urban runoff was the source of contamination, increased traffic use at Katy Field should have resulted in an increase in the concentrations of PAHs. As this was not the case, it brings into question the theory that urban runoff is responsible for the observed PAH distribution. Please note this in the report.

Response:

There have been many changes to the traffic patterns over the course of the period of 2002 through 2005. The installation of the overflow parking (gravel and stone) on the south end of Katy field in 2003 is actually a minor one because that lot has no storm drain connection. When this parking area was installed, a geofabric was laid down underneath which should have captured any abraded asphalt released. The most likely local influence of abraded asphalt to the storm drains would have been during demolition and construction of the parking areas around the former brig and current SWOS buildings, south of OFFTA. Finally, the decrease is clearly a result of the vortex interceptor system installed in line with the outfall 093, which will be clarified in the revised report.

44. Section 4.2, Petrogenic and Pyrogenic PAH Patterns., Paragraph 4.

This paragraph references a series of bar graphs (figures 4a-j). The y-axis on the histograms are not labeled. Please provide a label and an appropriate index for the y-axis.

Response:

The y-axis is concentration.

45. Section 4.2, Petrogenic and Pyrogenic PAH Patterns., Paragraph 4.

This paragraph notes that certain PAHs are associated with soot, while others are associated with asphalt, or diesel, etc. It is known that fuels contain a wide range of PAHs. Therefore, the report must explain why a PAH which may be found in several different fuels, can be assigned to a specific fuel or source.

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, the use of patterns of PAHs to indicate sources of materials and relative concentrations. Careful review and understanding of the new Attachment will address this comment.

46. Section 4.2, Petrogenic and Pyrogenic PAH Patterns., Paragraph 7.

The report notes that the petrogenic distribution of kerosene, diesel and crude oil when compared to the pyrogenic dominated composition of the site samples is proof of the source of contamination. As noted in the above comments, this comparisons and conclusion is flawed for the following reasons: 1) Only a limited number of fuels were used in the comparisons, while a wider variety of fuels would have been used at the site. As an illustration, Navy Special would have been used since it was the major fuel used for all surface ships. 2. All of these fuels would have been exposed to heat and fire, thus these fuels would have generated signatures corresponding to heat exposure and combustion (pyrogenic signatures). 3. This mixture of unburnt fuels and burnt fuels would have been exposed to both physical, chemical and biological decomposition. 4. The study failed to produce chromatograms for the above and therefore did not perform

any comparison. Therefore, by limiting the comparison to a few fuels and not considering the above, meaningful conclusions cannot be drawn. Therefore, please remove the conclusions presented in this section of the report.

Response:

On the contrary, the conclusions are supported by the science behind the report. Additional information will be added for clarity, and to address the points numbers above:

- 1) Additional reference material will be added to the comparisons and will include motor oil, and heavy fuel oils. Navy special is No. 5 oil, and would have been a poor candidate for fire training due to its difficulty to ignite. Regardless, the addition of these additional reference material descriptions to the revised report will support the conclusions already made.
- 2) The statement that "all fuels" would have been exposed to heat is a presumption. Fuel could have been lost before use in training, during storage, or transfer to and from delivery vehicles and burn chambers. In addition, after the fire is extinguished, it is likely that the fuel continued to flow until the exercise was completed. Regardless, pyrogenic signatures are evaluated in this report in detail, in Section 4.2, and such patterns are presented in Figures 4a – 4j. Chromatograms are presented in Attachment F.
- 3) The statement that the mixture of burnt and unburnt fuels would have been exposed to physical, chemical and biological decomposition is not argued. This is correct, and is addressed in the report.
- 4) Chromatograms for soils at OFFTA were provided in the 2002 report. Additional evaluations of soil will be provided in the revised 2005 report. The additional reference material will be added to the revised report as well. The conclusions are correct based on the data presented as stated.

**47. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Paragraph 8/9**

The section deals with PCA. The report must include a detailed discussion of PCA and how it was applied to the site. Further, in the main body of the test the report should provide an example of how PCA was applied to one sample. In an appendix the PCA applications details must be provided for each sample. Without this information it is not possible to determine whether PCA was applied correctly to the site samples.

Response:

An additional Attachment will be added to the forensic report, Attachment H, which is an overview of the process followed for the work conducted, including the role of PCA analysis. The addition of the new Attachment will address this comment.

**48. Section 4.2, Petrogenic and Pyrogenic PAH Patterns.,
Foot note**

This section of the report notes that the data is log transformed to account for variability in PAH concentrations between samples and the concentrations of between analytes. This approach would negate the importance of an analyte which was found in high concentrations while at the same time increase the importance of an analyte, which was found at low concentration or at trace levels, thereby generating erroneous conclusions. In order to avoid this problem, concentrations must be considered and log transformations should not be carried out.

Response:

Please refer to the response to Comment 41, above.

**49. Section 4.3, Fugitive Petroleum and Plant Wax s,
Whol Section**

In this section the origins of the observed contaminant distribution in the various sediment samples were assigned to different sources (diesel, asphalt, plant waxes). However justification for the claims made in this section was not provided. That is, if the report claims that a particular chromatogram represents diesel which has evaporated as opposed to biodegraded, in support of this position, chromatograms of evaporated and biodegraded diesel samples must be provided.

Response:

An additional Attachment will be added to the forensic report, Attachment I, which is a discussion of the soil samples collected and degradation, compared with suitable reference materials. The addition of the new Attachment will address this comment.

**50. Section 4.3, Fugitive Petroleum and Plant Waxes,
Whole Section**

The report states that all of the sediment samples are similar to SD 5. A review of the chromatograms indicates that this is not the case (some chromatograms have pronounced UCM, others do not, peak distribution and intensities are different, etc.) As there are considerable differences in the chromatograms, please remove these statements indicating that the chromatograms are similar and provide a more detailed explanation on why there are differences.

Response:

The fifth paragraph of Section 4.2 of the report states that samples at the OFFTA shoreline resemble the hydrocarbon mixture found in SD 5. The reviewer should keep in mind that this is only one line of evidence evaluated in the report. The text clearly also describes the differences and why those differences are likely to exist.

**51. Section 4.3, Fugitive Petroleum and Plant Waxes,
Whole Section**

The Navy has interpreted the saturated hydrocarbon fingerprint from the various samples collected at the site and included the following: Sample 75 is composed of plant wax, middle and heavy end petroleum distillate is not present, diesel is not present, and the plant wax contribution was so high that it masked any contribution from asphalt. The report states that chromatogram interpretation corresponds to field conditions as 75 has more plant material than the other catch basins. Sample 93 contains diesel and heavy end petroleum products, and plant waxes are not present. Again the report notes that the chromatogram interpretation corresponds to field observations, i.e. little vegetation next to 93 compared to 75. Finally 75a contains diesel, and asphalt with lower levels of plant waxes, again reflecting conditions observed in the field.

The actual site conditions bring into question the interpretations of the chromatograms in this report. Sample 75, which is composed of plant waxes with no asphalt or diesel, is located in the middle of a large asphalt parking lot. As such, it should have the highest concentration of asphalt and or diesel. Conversely sample 93, which has diesel and high-end petroleum, with no plant waxes and no asphalt PAHs identified in the chromatogram, abuts a grass field and a road. Therefore, it should have had both asphalt and plant waxes, the laer at concentrations far greater than sample 75. Finally, 75a is completely surround by grass, it is in the middle of Katy field. Accordingly, it should have had the highest concentration of plant waxes, and the lowest concentration of asphalt.

The fact that the assigned PAH distribution for the chromatograms does not correspond to site conditions brings into question the interpretation of the chromatograms and the process by which peaks are assigned to different potential sources. The chromatograms must be examined again using different protocols or procedures than that employed during this analysis.

Response:

The comment above reflects observations that are out of date. At the time of collection (February 2005), the sample described above named "Sample 75" was taken from a new catch basin installed for the SWOS in an area of landscaped topsoil, which had been hydroseeded. As it happened, the seed had been placed late in 2004, and a good quantity of the plant matter associated with the hydroseed appeared to have been washed into the storm drain by the time the sampling had been conducted.

The sample identified as "Sample 75a" was surrounded by what is no longer a grassy field – the topsoil had been removed almost 12 months prior to sampling for the purposes of removing the mounds at the site. The accessway had been blocked with geotextile to prevent intrusion of soil and grass from this construction action.

The sample identified as "Sample 93" also was within this construction area, and was blocked with geotextile, the trees formerly in this area had been removed in 2004.

**52. Section 4.4, Genetic Origins of Heavy Hydrocarbons,
Paragraph 3**

This section of the report notes that the genetic fingerprint indicates that there is contamination associated with heavy petroleum in the storm drain, yet this contamination is not observed in the sediment samples at the discharge point of the drain. Please explain why heavy petroleum contamination is observed in a drain, but is not observed at the outfall.

Response:

Review of the paragraph cited and the figures 7a -7d shows that "Pattern A" is shown in the debris sample, the catch basin sample 75a, the reference sample at Jamestown and the sample at the discharge point of the drain. This pattern is "a heavy residual petroleum product".

**53. Section 4.4, Genetic Origins of Heavy Hydrocarbons,
Paragraph 3**

This section of the report states that the two storm drains exhibit different genetic markers due to differences in the type of petroleum asphalt. The storm drains are in relatively close proximity to each other and service essentially the same area. If asphalt was the source of the PAH distribution, the chromatograms should have been the same. The fact that there are differences suggests another source other than asphalt. Please modify the report to reflect this potential for another source.

Response:

The report correctly cites possibilities of different asphalt materials in different areas laid at different times. The conclusions are made based on a preponderance of evidence described and they will not be revised unless new data shows different findings.

54. Reference Section.

The last two references refer to an article from Environmental Science and Technology (which could not be retrieved from the web) and a study conducted at the Norfolk Navy shipyard. Please provide a copy of these reports to the State.

Response:

The requested documents (Stout et al 2004 and Stout, et al for SPARWAR 2003) are provided attached to this response summary.

Comparative Evaluation of Background Anthropogenic Hydrocarbons in Surficial Sediments from Nine Urban Waterways

SCOTT A. STOUT,*†
ALLEN D. UHLER,† AND
STEPHEN D. EMSBO-MATTINGLY†
*Battelle Memorial Institute, 397 Washington Street,
Duxbury, Massachusetts*

Anthropogenic hydrocarbons in surficial urban sediments derived from nonpoint sources (e.g., stormwater runoff, surface runoff, direct atmospheric deposition, and small but persistent discharges) are the principal characteristics of "urban background". Establishing the character and concentration of urban background helps determine the incremental impacts from point sources and develop successful remedial strategies. In this study, we compared the nature and amount of total extractable hydrocarbons (THC) and polycyclic aromatic hydrocarbons (PAHs), including alkylated PAHs, within 280 surficial (mostly 0–10 cm) sediments from nine, well-studied urban waterways on the East and West U.S. Coasts. These 280 sediments were predominantly impacted by urban background. All the sediments were analyzed by consistent preparation and analytical methods and met consistent data quality objectives, thereby minimizing variations attributable to methodology. The data demonstrate that the anthropogenic hydrocarbons comprising urban background from all locations exhibit a generally consistent nature, dominated by (1) a variably shaped unresolved complex mixture (UCM) within the residual ($C_{20}+$) range and (2) a variable distribution of resolved 4- to 6-ring nonalkylated (parent) PAHs, mostly dominated by fluoranthene and pyrene (and exhibiting a FL/PY ratio of 0.9 ± 0.2). The variable nature of both the THC and PAH distributions testifies that, while there is a *general* consistency to urban background, there are definite differences between (and even within) different urban settings. This indicates that there is no single "representative" urban background THC or PAH signature. The greatest mass of THC is reasonably attributable to heavy petroleum-(s) comprising the UCM, whereas the greatest mass of PAHs is reasonably attributable to combustion-derived particulate matter. The mean concentration of THC attributable to urban background was 415 mg/kg (dry wt). The concentration of EPA 16-Priority Pollutant PAHs was less than 20 000 $\mu\text{g/kg}$ (dry wt) in 96% of the sediments studied. Thus, sediments containing significantly more than 20 800 $\mu\text{g/kg}$ of the EPA 16 Priority Pollutant PAHs (or more the 30 000 $\mu\text{g/kg}$ of 43 parent and alkylated PAHs) should be suspected to contain PAHs not entirely

attributable to urban background, unless site- or regional-specific survey data supports a different urban background concentration profile.

Introduction

Background concentrations of polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in freshwater and marine sediments worldwide. Low concentrations of naturally occurring background PAHs, derived from natural fires, natural oil-seeps, eroded shales/coals, and early diagenetic processes, pre-date modern anthropogenic activities (1, 2). However, the prolific use of fossil fuels by human civilization over the last 200 years has altered the loading of hydrocarbons to the environment. The resulting residues and combustion byproducts from these fuels have contributed a modern "anthropogenic background" to sediments in both urban (3, 4) and remote locations (5, 6). In water bodies near urban areas, the anthropogenic background PAHs are collectively called "urban background". They are derived from a variety of nonpoint sources such as (1) stormwater runoff (7), (2) direct deposition (atmospheric fallout) of combustion particles (soot) from biomass, coal, or petroleum combustion (8), (3) surface runoff from proximal roadways, parking lots, and bridges, or (4) discharges or spillage of unburned petroleum from boat/ship traffic. In most urban environments, stormwater runoff is probably the largest chronic contributor of anthropogenic background PAHs to urban sediments (3, 4, 9). Stormwater runoff and the other nonpoint sources often enter a waterway for decades and can impart recognizable profiles of anthropogenic background PAHs to urban sediments (10–12).

Understanding and determining the concentrations and distributions of anthropogenic background PAHs in sediments may help recognize PAH sources derived from specific point sources in urban waterways and coastal areas where multiple point sources typically coexist with persistent nonpoint, background sources (13). Common point sources of PAHs in many urban waterways include spilled or seeped petroleum products or coal- or oil-derived tars and their associated distillation products (e.g., creosote). The PAHs from these and other point sources are almost always "superimposed" on the PAHs derived from nonpoint sources representing the urban background. Recognizing background concentrations of PAHs is also critical in development of remediation strategies, which must consider the potential for "recontamination" of sediments due to the persistent influx of anthropogenic background PAHs.

This paper compiles, summarizes, and compares the nature and concentrations of urban background-derived PAHs in sediments from nine U.S. harbors and waterways recently studied (Table 1). By establishing the nature and variations in the concentrations and distributions of PAHs in these urban sediments, this paper facilitates the recognition of sediments impacted by PAHs derived from nonbackground, "point" sources.

Samples and Experimental Methods

The sediments evaluated in this study were collected and analyzed over the course of nearly 4 years (Table 1). All samples were obtained from the upper 20 cm of sediment gravity cores or upper 10 cm of Van Veen-type surface grab samples, with 95% of the samples evaluated having been obtained from the 0 to 10 cm interval. The laboratory adhered closely to similar sample preparation, analytical methods,

* Corresponding author phone: (781)681-5040; fax: (781)681-5048; e-mail: sstout@newfields.com.

† Current address for all authors: NewFields, 100 Ledgewood Place, Suite 302, Rockland, MA 02370.

TABLE 1. Inventory of Locations and Urban Background-Impacted Sediments Considered Herein

urban waterway/waterbody	year of study	n ^a
Boston Harbor, MA (Channel/Drydock Study)	1999	8
Boston Harbor, MA (CSO Study)	2002	53
Eagle Harbor, Bainbridge Island, WA	2000	26
Elizabeth River, Norfolk, VA	2002	22
Long Island Sound, NY	2002	12
Portland Harbor, Portland, OR	2001	23
Quantico Marine Corps Base, Quantico, VA	2002	9
Rhode Island Sound, RI	2002	41
San Francisco Bay, Alameda Pt., CA	2001	57
San Francisco Bay, various reference locations, CA	2000	12
Thea Foss Waterway, Tacoma, WA	1999	17

^a n = number of samples representing background.

and data quality control indicators (e.g., surrogate and spike recoveries ranged from 80 to 120%, duplicate relative percent differences were less than 20%, and procedural blanks contained no detectable PAH analytes). Consequently, these data were highly comparable and minimally biased by procedural or analytical artifacts. The methods employed included serial extraction of the surrogate-spiked sediments using dichloromethane, alumina column cleanup of the extract, and treatment with copper sulfate according to modified EPA Methods 3550, 3611, and 3660, respectively. The extracts were then concentrated, spiked with appropriate internal standards, and analyzed for total extractable hydrocarbons (THC) via a modified EPA Method 8015 and PAHs via a modified EPA Method 8270. These methods have been previously described (14, 15, 17). Notably, the PAH analytes included up to 43 nonalkylated (parent) and alkylated PAHs (including sulfur-containing dibenzothiophenes) (Table 2) that reliably distinguished one or more sources of PAHs (including urban background) in past sediment investigations (2, 18–20). Not every sediment was analyzed for THC via modified EPA Method 8015 due to individual project needs.

The available data from each study were reviewed to eliminate sediments that were impacted by various point sources of PAHs. The basis for determining impacts from point sources included the following: (1) qualitative "pattern recognition" approach that included visual inspection of the available modified Method 8015 gas chromatograms (GCs) of the THC and PAH histograms, including comparison to reference materials, e.g., including known hydrocarbon

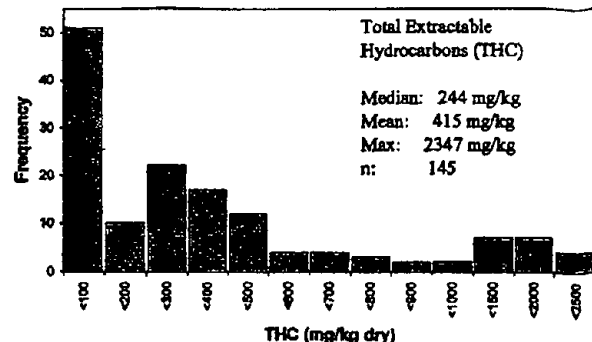


FIGURE 1. Histogram showing the distributions and concentrations of total extractable hydrocarbons (THC) in 145 sediments containing nonpoint sourced, background hydrocarbons.

sources (17) and contamination from proximal, upland point sources, (2) semiquantitative graphical analysis of PAH concentration data using source-specific diagnostic ratios or indices (e.g., cross-plots or ternary diagrams), again, sometimes including comparisons to reference materials (as above), (3) spatial and temporal analysis of PAH signatures and concentrations, including a comparison to historical information compiled for the area (e.g., operational history, aerial photos, etc.), and/or (4) quantitative chemometric analysis involving numerical analysis methods such as principle component analysis (PCA; e.g., ref 20).

This data review resulted in a subset of sediments from each study that was believed to have been impacted by urban background alone (see "n" in Table 1). While this review was probably not error-free, it minimized the potential for including sediments containing significant levels of PAHs derived from point sources not reasonably attributable to urban background.

Results and Discussion

The total extractable hydrocarbon (THC) concentrations in the 145 sediments studied by modified EPA Method 8015 ranged from 8 to 2350 mg/kg (dry), with a mean and median concentration of 415 and 244 mg/kg, respectively. Most (77%) of the urban sediments impacted by background hydrocarbons contained less than 500 mg/kg THC (Figure 1).

The chromatographic character of THC from most sediments exhibited similar gross features and illustrates the overall similarity in the nature of urban background in different urban settings. Figure 2 shows the EPA Method 8015 gas chromatograms of the THC for four sediments from different urban areas. All of the sediments exhibit two characteristic chromatographic features, viz., (1) numerous

TABLE 2. Inventory of PAHs Commonly Used To Distinguish PAH Sources

analyte	abbr.	ring #	cat. ^a	analyte	abbr.	ring #	cat. ^a	analyte	abbr.	ring #	cat. ^a
naphthalene ^a	N0	2	petro	C1-phenanthrenes/anthracenes	P1	3	mixed	benz[a]anthracene ^a	BaA	4	pyro
C1-naphthalenes	N1	2	petro	C2-phenanthrenes/anthracenes	P2	3	petro	chrysene ^a	C0	4	pyro
C2-naphthalenes	N2	2	petro	C3-phenanthrenes/anthracenes	P3	3	petro	C1-chrysenes	C1	4	pyro
C3-naphthalenes	N3	2	petro	C4-phenanthrenes/anthracenes	P4	3	petro	C2-chrysenes	C2	4	petro
C4-naphthalenes	N4	2	petro	Dibenzothiophene	D0	3	petro	C3-chrysenes	C3	4	petro
biphenyl	Bph	2	petro	C1-dibenzothiophenes	D1	3	petro	C4-chrysenes	C4	4	petro
acenaphthylene ^a	Acl	3	petro	C2-dibenzothiophenes	D2	3	petro	benzo[b]fluoranthene ^a	BbF	5	pyro
acenaphthene ^a	Ace	3	petro	C3-dibenzothiophenes	D3	3	petro	benzo[k]fluoranthene ^a	BkF	5	pyro
dibenzofuran	DdF	3	petro	C4-dibenzothiophenes	D4	3	petro	benzo[e]pyrene	BeP	5	pyro
fluorene ^a	F0	3	petro	fluoranthene ^a	FL	4	pyro	benzo[a]pyrene ^a	BaP	5	pyro
C1-fluorenes	F1	3	petro	pyrene ^a	PY	4	pyro	perylene	Per	5	bio
C2-fluorenes	F2	3	petro	C1-fluoranthenes/pyrenes	FP1	4	pyro	indeno[1,2,3-c,d]pyrene ^a	ID	6	pyro
C3-fluorenes	F3	3	petro	C2-fluoranthenes/pyrenes	FP2	4	petro	dibenz[a,h]anthracene ^a	DA	5	pyro
anthracene ^a	AN	3	pyro	C3-fluoranthenes/pyrenes	FP3	4	petro	benzo[g,h,i]perylene ^a	BgP	6	pyro
phenanthrene ^a	P0	3	mixed								

^a EPA priority pollutant. ^b petro = petrogenic (30). pyro = pyrogenic (30).

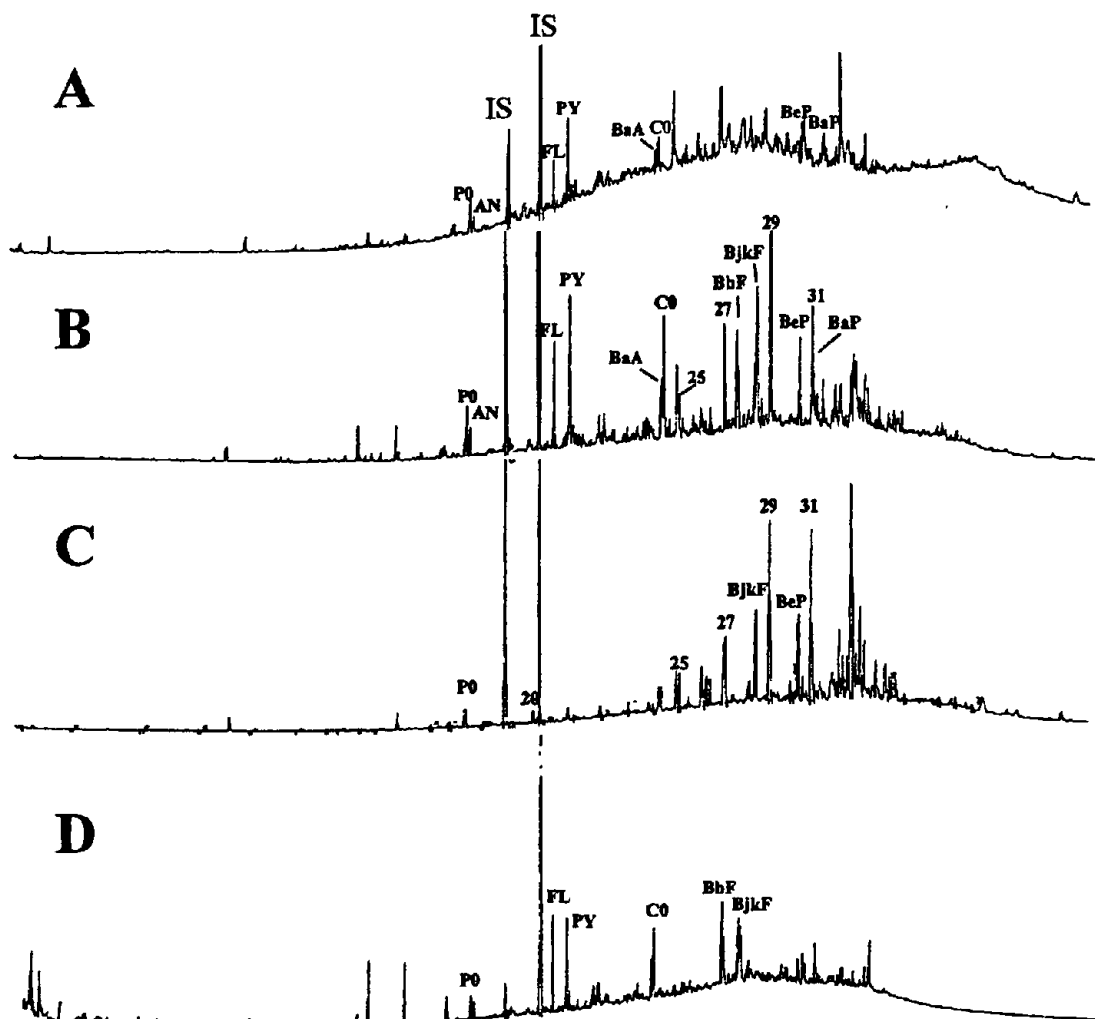


FIGURE 2. GC/FID chromatograms for extractable hydrocarbons for sediments impacted by urban background in the following: (A) Thea Foss Waterway, (B) Eagle Harbor, (C) Portland Harbor, and (D) Elizabeth River sites (Table 1). IS — internal standards. See Table 2 for PAH peak identifications. # — *n*-alkane carbon numbers.

later-eluting resolved peaks and (2) an unresolved complex mixture (UCM) "hump" mostly within the residual ($C_{20}+$) oil range. Previous studies observed many of these gross features in urban background sediments from many areas (3, 21–23). The resolved peaks represent various nonalkylated 4- to 6-ring PAHs (high molecular weight PAHs or HPAHs), which are indicative of the combustion-derived particles in engine exhaust (2, 24, 25). The residual range UCM hump is comprised of (mostly) branched and cyclic hydrocarbons that occur in heavy petroleum (i.e., lubricating, hydraulic, waste oil, and asphalt), which is an expected component within urban runoff (26). Although quantitative data are not available to distinguish the resolved versus unresolved THC mass for most of the samples studied, it is apparent that the UCM contains the dominant mass of the background hydrocarbons found in the urban sediments studied. Also present in some urban sediments (Figure 1B,C) are numerous odd carbon number-dominated normal alkane hydrocarbons ($n-C_{27}$, $n-C_{29}$, $n-C_{31}$) indicative of plant waxes derived from modern leaf debris in the sediments (27, 28). These biogenic *n*-alkanes represent only a small proportion of the mass of hydrocarbons in most urban sediments.

Despite the gross similarity in the character of the THC among these urban sediments, differences exist; e.g., the shapes of the UCM's and specific distributions of HPAHs vary (see below). These differences are testimony to fact that

there is no single representative THC chromatographic "fingerprint" indicative of urban background. Instead, urban background represents a range of hydrocarbons only generally exhibiting the features described above.

The distribution of parent and alkylated PAHs (Table 2) in most of the sediments studied also exhibit only a general similarity. Figure 3 shows the PAH histograms for selected sediments from six of the locations studied. As expected, each sediment is dominated by HPAHs, the most abundant of which are (with few exceptions; e.g. Figure 3B) fluoranthene and pyrene. Interestingly, the sediments exhibit marked variations in the distribution among other prominent HPAHs, which along with the variable UCM shapes described above (Figure 1), further illustrates the variable nature of urban background from different regions. These differences are described in greater detail below. Each PAH homologue series shown demonstrates a decreasing abundance with increasing degree of alkylation (i.e., a skewed pattern), as is typical of pyrogenic PAHs (2, 14). It is on this basis that urban background is described as a "pyrogenic" source of PAHs, despite a significant petroleum contribution on a total mass basis (e.g., as is evidence by the UCM; Figure 1).

Figure 3G shows the median concentrations (and 25th and 75th percentiles) for all 280 sediments included in this study (Table 1). The similarity in the PAH distribution between the median values (Figure 3G) and the selected sediments

TABLE 3. Population Statistics for PAH Concentrations and Diagnostic Indices for Sediments Impacted with Urban Background*

		Rhode Island Sound	Quantico, VA	SF Bay Ref. Sites	Long Island Sound	Portland Harbor	Alameda Pt., CA	Boston Harbor (DD/Ch)	Thos Foss, WA	Eagle Harbor, WA	Boston Harbor (CSO)	Elizabeth River	All sites
	n	41	9	12	12	23	87	8	17	26	53	22	280
PAH _{total} priority pollutant only (Table 2)	mean	240	741	1,006	1,880	2,829	3,083	8,816	11,278	11,429	9,484	15,914	6,086
	med	55	713	1,113	1,699	2,045	2,725	7,747	10,654	10,993	8,640	18,080	3,262
	SD	661	434	511	1,011	3,008	1,712	4,790	2,482	9,745	9,159	7,324	7,442
	min	8	205	195	941	419	849	966	7,861	5,129	275	5,036	8
	max	4,256	1,306	168	4,844	13,636	8,440	15,013	18,962	51,373	42,545	36,925	51,373
PAH _{total} Σ ₄₅ (Table 2)	mean			1,517		4,686	4,382		19,860	17,517	14,870	25,502	11,965
	med			1,688		3,198	3,847		18,569	12,742	10,962	26,268	8,129
	SD	NA ^c	NA ^c	708	NA ^c	4,572	2,371	NA ^c	4,215	15,084	14,146	11,215	12,367
	min			407		860	751		14,934	8,524	406	8,728	406
	max			2,482		20,644	11,059		29,530	80,913	67,855	58,902	80,913
%PAH as Priority Pollutant PAH	mean			64.6		57.0	70.7		56.7	65.1	62.9	61.8	64.1
	med			67.2		59.3	71.4		57.5	65.0	64.3	63.1	65.0
	SD	NA ^c	NA ^c	10.8	NA ^c	8.3	3.7	NA ^c	2.0	1.8	5.8	3.9	7.1
	min			30.9		43.7	58.0		52.8	60.2	38.2	47.5	30.9
	max			71.5		71.4	77.3		59.4	68.0	71.8	65.4	77.3
COC2	mean			4.08		2.92	3.84		2.80	5.02	3.41	3.59	3.68
	med			3.91		3.08	3.78		2.86	4.75	3.41	3.66	3.48
	SD	NA ^c	NA ^c	1.30	NA ^c	0.98	1.17	NA ^c	0.47	1.53	0.87	0.98	1.24
	min			1.80		1.07	1.03		1.97	2.88	1.41	1.86	1.03
	max			6.55		4.55	8.79		3.41	8.61	8.20	5.32	8.61
LPAH/HPAH	mean			0.36		0.44	0.23		0.51	0.28	0.46	0.20	0.34
	med			0.25		0.40	0.23		0.51	0.27	0.45	0.18	0.29
	SD	NA ^c	NA ^c	0.39	NA ^c	0.13	0.05	NA ^c	0.07	0.07	0.14	0.07	0.17
	min			0.20		0.21	0.11		0.39	0.16	0.23	0.13	0.11
	max			1.59		0.69	0.40		0.66	0.48	0.91	0.47	1.59
AN/P0	mean	0.19	0.24	0.28	0.29	0.27	0.38	0.43	0.65	1.10	0.33	1.20	0.47
	med	0.2	0.27	0.28	0.28	0.27	0.37	0.43	0.63	1.01	0.34	1.13	0.34
	SD	0.07	0.09	0.08	0.02	0.06	0.08	0.06	0.06	0.25	0.08	0.45	0.38
	min	0.1	0.1	0.11	0.27	0.17	0.2	0.27	0.54	0.68	0.17	0.54	0.10
	max	0.45	0.36	0.45	0.93	0.45	0.6	0.55	0.79	1.81	0.48	1.97	1.97
FL/PY	mean	1.11	1.02	0.77	0.87	0.84	0.78	1.03	0.71	0.59	1.05	0.97	0.81
	med	1.13	1.02	0.76	0.87	0.93	0.77	1.04	0.72	0.58	1.07	1.00	0.83
	SD	0.11	0.11	0.05	0.07	0.11	0.12	0.14	0.04	0.18	0.07	0.19	0.20
	min	0.83	0.9	0.71	0.72	0.76	0.42	0.83	0.62	0.15	0.83	0.66	0.15
	max	1.32	1.24	0.91	1.04	1.18	1.3	1.18	0.76	1.07	1.20	1.25	1.32
Ba/Co	mean	1.11	0.67	0.83	1.00	0.75	0.82	0.88	0.70	0.59	0.87	0.58	0.83
	med	0.75	0.71	0.87	0.99	0.76	0.83	0.90	0.70	0.58	0.87	0.57	0.80
	SD	0.86	0.12	0.11	0.08	0.08	0.07	0.06	0.07	0.08	0.07	0.08	0.37
	min	0.004	0.41	0.52	0.87	0.56	0.59	0.77	0.53	0.44	0.72	0.44	0.33
	max	3.15	0.81	0.95	1.22	0.86	1.03	0.96	0.79	0.77	1.03	0.78	3.15
BbF/BkF	mean	2.02	1.23	3.64	2.92	1.07	1.05	1.04	1.12	1.13	1.05	1.28	1.42
	med	1.04	1.21	3.66	2.65	1.07	1.05	1.02	1.12	1.16	1.03	1.25	1.10
	SD	1.77	0.15	0.39	0.15	0.07	0.08	0.08	0.07	0.13	0.10	0.08	0.85
	min	0.45	1.06	2.90	2.67	0.96	0.9	0.94	1.04	0.84	0.85	1.12	0.45
	max	7.24	1.47	4.25	3.18	1.24	1.31	1.17	1.3	1.34	1.27	1.44	7.24
BeP/BaP	mean			0.75		0.76	0.61		0.78	0.93	0.74	1.00	0.78
	med			0.68		0.71	0.61		0.76	0.94	0.73	0.89	0.72
	SD	NA ^c	NA ^c	0.28	NA ^c	0.10	0.04	NA ^c	0.05	0.05	0.06	0.25	0.17
	min			0.60		0.60	0.52		0.65	0.80	0.62	0.79	0.62
	max			1.63		0.93	0.77		0.83	1.01	0.89	1.75	1.75
ID/BgP	mean	0.96		0.89	1.18	0.92	0.95	1.01	1.07	1.15	1.13	1.09	1.03
	med	0.96		0.89	1.17	0.91	0.94	1.01	1.06	1.16	1.09	1.10	1.04
	SD	0.10	NA ^c	0.05	0.04	0.04	0.06	0.03	0.04	0.04	0.11	0.05	0.12
	min	0.71		0.82	1.12	0.82	0.83	0.86	1.04	1.07	0.86	0.86	0.71
	max	1.16		1.00	1.29	0.99	1.15	1.05	1.17	1.21	1.59	1.16	1.59
% Petrogenic PAH ^b	mean			23.8		32	18.7		33.1	22.9	29.6	22.4	27.6
	med			20.9		28.6	18.2		32.4	21.9	30.0	20.9	25.6
	SD	NA ^c	NA ^c	11.8	NA ^c	8.4	3.94	NA ^c	2.9	2.97	5.8	4.72	7.5
	min			17.8		18.8	10.8		28.9	18.4	19.1	17.3	13.0
	max			60.3		45.1	32.1		39.8	30.4	42.7	39.7	64.2
% Pyro-genic PAH ^b	mean			79.4		71.7	83.5		68.1	78.8	70.4	78.2	72.4
	med			82.8		74.2	84.1		68.0	78.8	70.0	80.6	74.4
	SD	NA ^c	NA ^c	12.1	NA ^c	7.67	4.05	NA ^c	2.94	3.17	5.6	4.83	7.5
	min			41.1		57.1	69.9		61.4	70.5	57.3	61.8	35.8
	max			85.5		83.9	91.8		72.4	83.2	80.9	84.2	87.0

* All concentrations in µg/kg dry wt. ^b See Table 2 for PAH category. ^c NA – missing PAH analytes precludes calculation.

shown (Figure 3A–F) further demonstrates the overall similarity in the distribution of PAHs in sediments impacted by urban background, i.e., dominated by nonalkylated HPAHs, particularly fluoranthene and pyrene. As was the case with the THC, there is no single representative PAH

"fingerprint" indicative of urban background. Instead, the PAHs derived from urban background represents a range of patterns, as generally represented by Figure 3G.

Select population statistics related to the available PAH data for the 280 sediments from the nine study areas evaluated

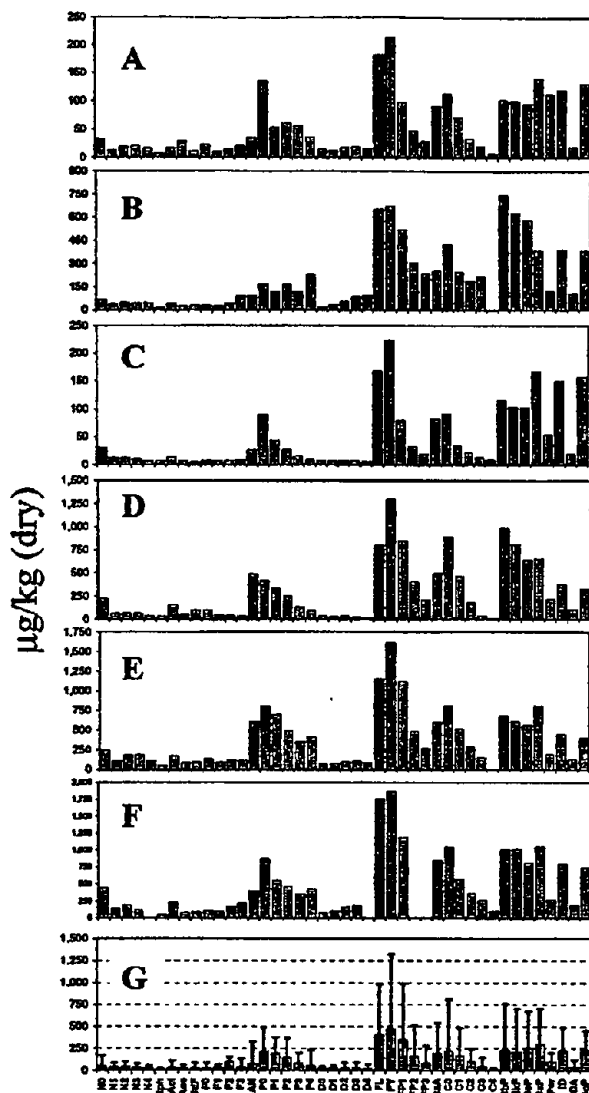


FIGURE 3. PAH histograms for selected sediments impacted with urban background from the following: (A) Portland Harbor, (B) Elizabeth River, (C) Alameda Point, (D) Eagle Harbor, (E) Thea Foss, (F) Boston Harbor (CSO study), and (G) median of all sediments studied. Error bars demonstrate 25th and 75th percentiles. For peak ID's see Table 2.

are summarized in Table 3. Inspection of Table 3 reveals some interesting regional variations among the nine sites investigated. This variation testifies to the difficulty of generalizing about the specific nature of background hydrocarbons in all urban environments. This variation is further investigated below.

The concentrations of the 16 EPA-Priority Pollutant PAHs and total PAH₁₆ (Table 2) for the sediments that were evaluated varied. The highly urbanized Elizabeth River (Virginia) study area had the highest concentrations of background PAHs, whereas the less urbanized Rhode Island Sound sediments contained the lowest concentrations (Table 3). Overall, the vast majority (96%) of the urban background-impacted sediments studied contained less than 20 000 µg/kg of the 16 EPA-Priority Pollutant PAHs (Figure 4A). Similarly, 96% of the sediments contained less than 30 000 µg/kg of total PAH₁₆ (Figure 4B). This result provides a reasonable "rule-of-thumb" for recognizing sediments that may contain PAHs derived from nonbackground (point) sources. For example, sediments containing approximately 20 000 µg/kg of the 16 Priority Pollutant PAHs are likely dominated by

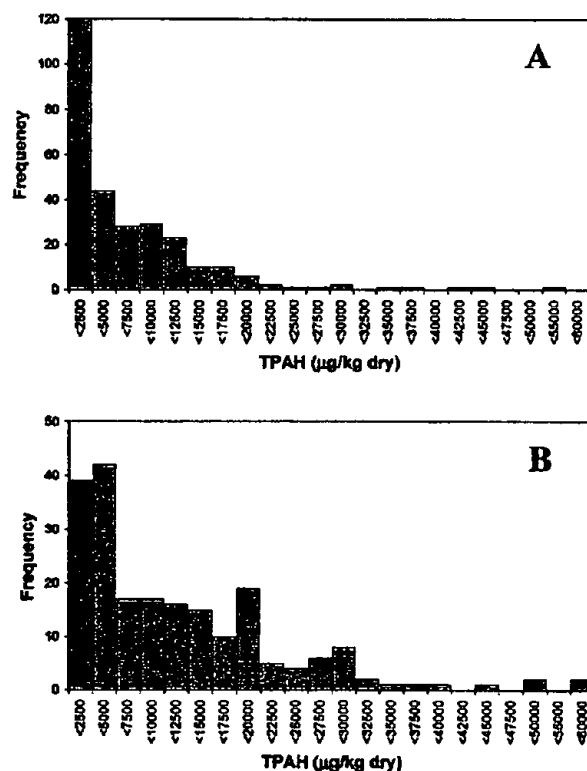


FIGURE 4. Histograms showing populations of PAH concentrations: (A) 16 priority pollutant PAH only and (B) sum of all 43 PAH analytes (Table 2). X-axis: max. concentrations in µg/kg dry weight.

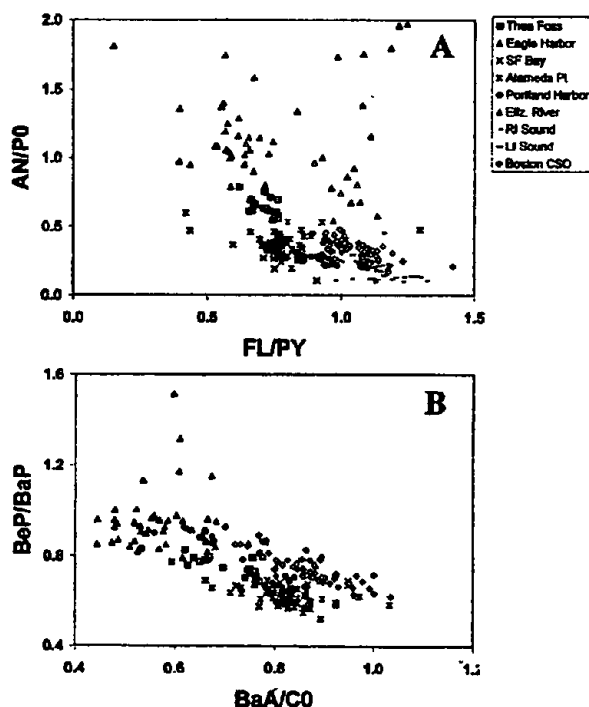


FIGURE 5. Double-ratio plots of selected PAH isomer ratios for sediments impacted by urban background: (A) fluoranthene/pyrene versus anthracene/phenanthrene and (B) benzo[a]anthracene/chrysene versus benzo[e]pyrene/benzo[a]pyrene.

urban background, while sediments containing significantly higher concentrations may indicate the additional PAHs contribution(s) of one or more point sources. Of course, because a small fraction of exceptions exists, this "rule-of-

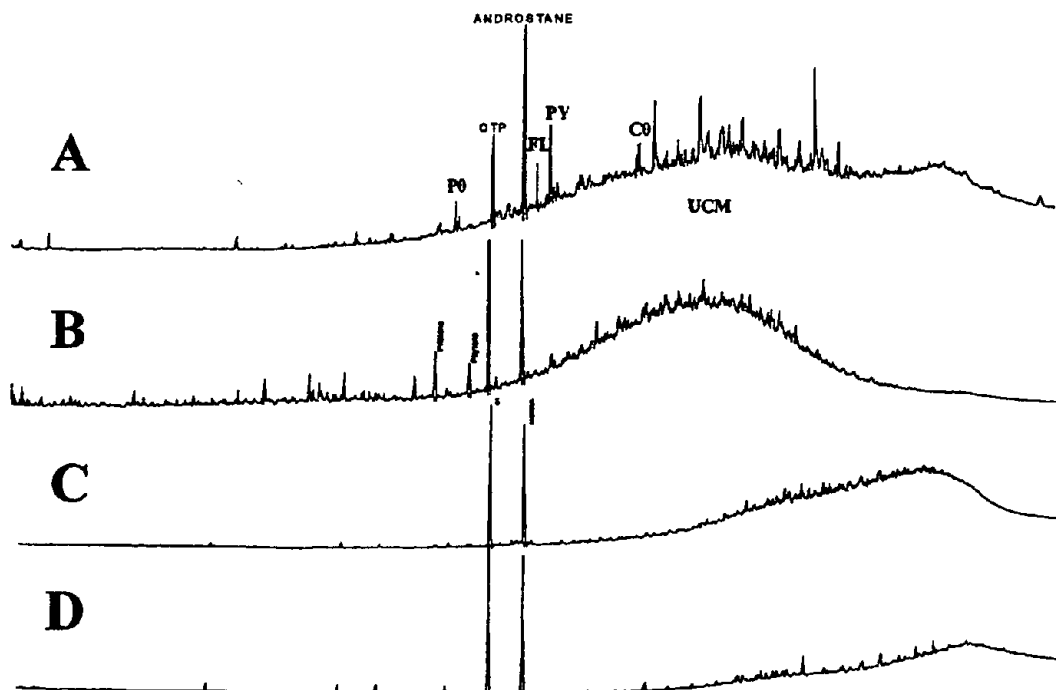


FIGURE 6. GC/FID fingerprints showing the chromatographic character of the UCM humps in (A) Thea Foss sediment impacted by urban runoff, (B) used motor oil, (C) used hydraulic oil, and (D) petroleum-based road asphalt. OTP and androstane are internal standards.

thumb" requires confirmation within any given study area and should not be applied blindly to limited numbers of samples.

The Priority Pollutant PAHs identified are all nonalkylated parent PAHs and predominantly "pyrogenic" in character (Table 2). The data assembled demonstrate that a consistently high percentage of total PAH_{24} exists as priority pollutant PAHs (56.7–70.7%; Table 3), which indicates the sediments contain an abundance of nonalkylated and mostly "pyrogenic" PAHs. This is evident in the skewed character of each PAHs homologues present in urban background (e.g., Figure 3). This predominance of nonalkylated parent PAH over their alkylated equivalents in sediments impacted by urban background is reflected in the consistently high ratios of chrysene to C2-chrysenes (2.80–5.02; Table 3).

Average ratios among various PAH isomers exhibit considerable variation among the different sites studied (Table 3). PAH isomer ratios are expected to vary with PAH source (12, 29) most likely due to the kinetics of PAH formation under different conditions (30). This variation suggests differences in the nature of the PAH background sources among the sites studied. Preferential weathering of one isomer over another also could contribute to the variation within a site, but weathering is unlikely to explain the variability observed between different sites. Therefore, interpretation of the cause(s) for the observed isomer differences requires a more detailed investigation than is possible in this data survey, but the causes for variability could include factors that affect (1) the source(s) type and strength (e.g., nearby land use, traffic volume) or (2) the transport and deposition dynamics (e.g., hydrographic and meteorological conditions (4)). (Recall, since all of these samples were analyzed by the same method in the same laboratory, the observed differences are not likely attributable to analytical artifacts.)

Notably, lower standard deviations, a measure of greater consistency among the data from each site, are observed for the isomer ratios of fluoranthene/pyrene (FL/PY; 0.93 ± 0.20) and indeno(1,2,3-*cd*)pyrene/benzo(ghi)perylene (ID/BgP; 1.05 ± 0.12 ; Table 3). This greater degree of consistency among

these particular isomer ratios could suggest a greater consistency in the source of these particular PAHs, e.g., a ubiquitous source such as petroleum combustion products from gasoline and diesel engines (31, 32).

Cross-plots of the PAH isomer ratios of FL/PY versus AN/P0 and BaA/C0 versus BeP/BaP are shown in Figure 5. Inspection of these plots reveals that isomeric distinctions exist among the different study areas. For example, the sediments from three study areas, viz., Thea Foss Waterway, Eagle Harbor, and Elizabeth River, exhibit AN/P0 ratios generally higher (>0.5) than sediments from the other locations (Figure 5A). These same three sites exhibit lower BaA/C0 and higher BeP/BaP ratios (Figure 5B). Although lesser distinctions can be observed among all of the sites, these three sites appear particularly exceptional among the sites studied. A common and unique feature among the Thea Foss Waterway, Eagle Harbor, and Elizabeth River study areas is that they each contained historic coal/oil tar production and processing operations. It is possible that the sediments in these three areas have been impacted by small amounts of "background" coal/oil tar or its products, which have contributed the ambient conditions in sediments from these waterways. In any case, it is interesting to observe that these PAH isomer ratios demonstrate differences among the background PAHs found in the different study areas (Figure 5). Such differences further emphasize the absence of a "typical" urban background signature universally present in all urban sediments.

Assessment of Sources of Hydrocarbons in Urban Background. While a thorough assessment of the THC and PAH apportionment for urban background sources is well beyond the scope of this survey, the variation in the character of urban background described above warrants some discussion as to the potential sources of THC and PAHs in the sediments. With respect to THC sources, as described above, the chromatographic character of THC comprising urban background generally exhibits two features, viz., (1) a UCM hump mostly within the C_{20+} hydrocarbon range and (2) numerous, later-eluting resolved hydrocarbon compounds. On a mass basis, the UCM generally contains the predominant background hydrocarbons (e.g., Figure 2). The UCM is

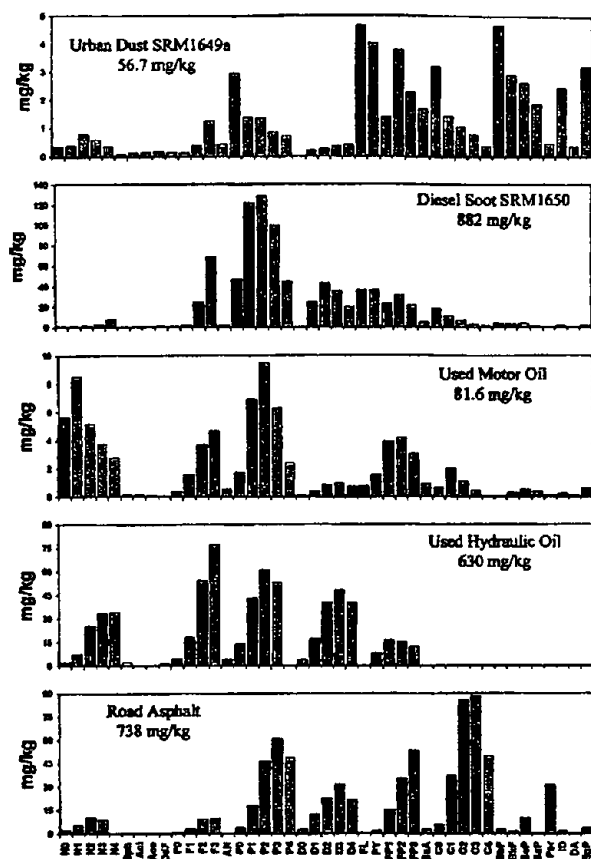


FIGURE 7. Histograms showing the distributions and concentrations of PAHs in various urban runoff candidate source components. For compound abbreviations see Table 2. Concentrations are in mg PAH per kg of sample material. Total concentrations shown are the sum of 43 analytes in Table 2.

generally attributed to petroleum-derived source materials (33). A prominent UCM is consistent with biodegraded petroleum, uncombusted petroleum, motor (crankcase) and hydraulic oils, or abraded asphalt (26, 34). All of these materials are potential components of urban runoff. Notice the specific shapes of the UCM "humps" in sediment samples from the different study areas (Figure 2). These differences may reflect site-specific (or even sample-specific) mixtures of heavy petroleum (e.g. heavy fuel oils, lubricating oils, asphalt) types. Figure 6 shows an example of the UCM hump for an urban runoff-impacted sediment from the Thea Foss Waterway, Tacoma, WA (35). The UCM in this particular sediment exhibits a bimodal character. The GC/FID chromatograms for used motor oil, used hydraulic oil, and road paving asphalt are shown for comparison (Figure 6B–D). The chromatograms for each of these heavy petroleum products are dominated by a characteristic UCM hump. It is easy to envision how these heavy petroleum products dripped from vehicles or abraded from road surfaces are washed from urban road surfaces during storm events before eventually entering the sediments and producing a broad, even bimodal, UCM hump (as appears in Figure 6A). Varying input of these and other ubiquitous, heavy petroleum-derived materials could produce the variably shaped UCM humps observed in many sediments containing urban background hydrocarbons (e.g., Figure 2).

The sources of background PAHs in urban runoff clearly vary, although most previous studies have long since and unanimously demonstrated that the PAHs in urban runoff are largely associated with combustion-derived particulate matter (9, 36–40). The PAHs associated with combustion-

derived particulate matter are complex mixtures dominated by higher molecular weight 4- to 6-ring, nonalkylated PAHs, as occur in motor exhaust (24), coal combustion products (29), or wood smoke (25, 41). Since these general features dominate the PAH profiles of sediments impacted by urban background (Figure 3 and Table 3), our data further support a combustion-derived particulate matter source of most PAHs. The distributions and concentrations of 43 PAHs in selected potential source materials (for which comparable data were available) affirm the pyrogenic origin of urban background PAHs (Figure 7). These candidate sources include PAHs found in urban dust (SRM 1649a; collected in 1976–1977 in Washington, DC), diesel exhaust soot (SRM 1650), used motor oil (Restek, Inc. Standard), used hydraulic oil, and petroleum-based road asphalt (17). A strong pyrogenic signature of the PAHs is evident in the urban dust, which certainly includes combustion-derived particulate matter, and this signature tends to most closely resemble the PAH profiles found in most urban sediments (compare to Figure 3). The diesel soot, used motor oil, used hydraulic oil, and road asphalt all exhibit strong petrogenic PAH signatures, but each of these exhibits a distinct distribution of PAHs. The greater resemblance between the PAHs in urban sediments (Figure 3) and urban dust (Figure 7) suggests that the latter is a predominant source of background PAHs in many urban sediments. This appears to be the case despite the generally low concentration of PAHs in urban dust compared to the other contributing sources (Figure 7). Although petrogenic PAHs are likely present as indicated by the UCM, the petroleum components of urban background contain low levels of PAHs relative to urban dust.

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Received for review January 12, 2004. Revised manuscript received March 17, 2004. Accepted March 31, 2004.

ES040327Q